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# Electron Exchange Correction to the Phonon Dispersion Relation in Metals

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This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NASw-6, sponsored by the National Aeronautics and Space Administration.



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# Electron Exchange Correction to the Phonon Dispersion Relation in Metals*

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The statistical theory recently developed is applied in this paper to an investigation of the dispersion relation of sound waves in metals with special regard to contributions due to electron exchange. It is found that these contributions are by no means negligible in the long-wavelength limit, contrary to current belief. Furthermore it is shown that the temperature dependence of the renormalized sound frequencies is solely mediated by the temperature dependence of the Fermi-Dirac distribution of the electrons.

## 1. INTRODUCTION

THIS paper constitutes a continuation of investigations of the interaction of electrons and phonons given in another paper.[1] The theory outlined there is essentially a statistical Hartree-Fock method. It is well known that the Hartree-Fock method consists in solving Schrödinger's equation for an $n$-particle system with the assumption that the total wave function splits into a (symmetrized) product of single-particle wave functions. In other words, each particle moves in the average field of all other particles. This of course leads to nonlinear equations if the method is to be self consistent. Precisely the same arguments may be invoked in the case where one deals with a statistical ensemble of particles. Now it is the distribution function or the density matrix of the $n$-particle system which is assumed to split into a (properly symmetrized) product of single-particle distribution functions or density matrices. The at first linear Liouville equation then becomes a nonlinear one and it goes over[2] into the classical collisionless Boltzmann equation in the transition $\hbar=0$.

Linearization leads to a set of equations which is entirely equivalent to the random-phase approximation.[3] In this paper we are going to derive a collisionless Boltzmann equation for the phonon gas of a metal using the theory as developed in I. This equation, after linearization, will yield the desired dispersion relations and it will be shown that a contribution arises from electron exchange which constitutes a correction of 10% for the velocity of sound in the limit of long wavelengths. Disregarding the exchange contribution, the well-known dispersion relation of Bardeen and Pines[4] is recovered. It will also be shown that the temperature dependence of the dispersion relation is rather weak and an excellent approximation is the use of the 0°K Fermi-Dirac distribution even at temperatures far from zero. In Sec. 3 the exchange correction will be computed for sodium and a comparison will be made with experiment.

## 2. DERIVATION OF THE DISPERSION RELATION

A determination of the dispersion relation for sound waves is most easily effected by eliminating the electronic degrees of freedom from the equation of motion of the phonons. According to I, the equation of motion for the Fourier transform of the perturbed electron distribution function is

$$\left(-w+\frac{\hbar}{m}\mathbf{K}\cdot\mathbf{k}+\frac{\hbar}{2m}K^2\right)\beta(\mathbf{K},\mathbf{k},w)$$
$$=w_P^2\frac{m}{\hbar K^2}\Delta F_0\int\beta(\mathbf{K},\mathbf{k}',w)d^3k'-w_P^2\frac{m}{2\hbar}\int d^3k'$$
$$\times|\mathbf{k}-\mathbf{k}'|^{-2}[\beta(\mathbf{K},\mathbf{k}',w)\Delta F_0-\beta(\mathbf{K},\mathbf{k},w)\Delta F_0']$$
$$-\frac{i}{(2\pi)^4}\frac{1}{\hbar}\phi(\mathbf{K})\Delta F_0\int dt\,e^{iwt}\sum_j\langle\Omega(t)|\mathbf{a}_j|\Omega(t)\rangle\cdot\mathbf{K}$$
$$\times\exp\{-i\mathbf{K}\cdot\mathbf{R}_j^0\}. \quad (1)$$

All symbols are the same as in I. $\Delta F_0$ is defined by

$$\Delta F_0=F_0(\mathbf{k}+\mathbf{K})-F_0(\mathbf{k}). \quad (2)$$

Equation (1) is equivalent to Eq. (18) of I, the only difference being that the static part of the electron ion interaction has been eliminated in a manner similar to the procedure in I. The equation of motion for the phonon-state vector $\Omega(t)$ is, according to I,

$$\left\{\hbar\sum_{\alpha\mathbf{Q}}w_\alpha(\mathbf{Q})b_\alpha^\dagger(\mathbf{Q})b_\alpha(\mathbf{Q})+N_1\sum_j\mathbf{a}_j\cdot\nabla_{R_j^0}\int d^3r'd^3k'\right.$$
$$\left.\times V(\mathbf{R}_j^0-\mathbf{r}')\tilde{F}_1(\mathbf{r}',\mathbf{k}',t)\right\}\Omega=i\hbar\dot{\Omega}, \quad (3)$$

where $\tilde{F}_1$ is the perturbed electron distribution function. The ionic displacements $\mathbf{a}_j$ may be expressed by the phonon creation and destruction operators in the

* This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract, sponsored by the National Aeronautical and Space Administration.

[1] O. von Roos, Phys. Rev. **120**, 1641 (1960), hereafter referred to as I.

[2] O. von Roos, Phys. Rev. **119**, 1174 (1960).

[3] We cannot attempt to give a complete list of references here but will instead only quote one paper which seems to be the earliest and most significant in this field: D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

[4] J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

well-known manner:

$$\mathbf{a}_j=\left(\frac{\hbar}{2MN}\right)^{\frac{1}{2}}\sum_{\alpha,\mathbf{Q}}[w_\alpha(\mathbf{Q})]^{-\frac{1}{2}}\mathbf{e}_\mathbf{Q}^{(\alpha)}$$
$$\times\{\exp[i\mathbf{Q}\cdot\mathbf{R}_j^0]b_\alpha(\mathbf{Q})+\exp[-i\mathbf{Q}\cdot\mathbf{R}_j^0]b_\alpha^\dagger(\mathbf{Q})\}. \quad (4)$$

The $\mathbf{e}_\mathbf{Q}^{(\alpha)}$ are unit vectors such that

$$\mathbf{e}_\mathbf{Q}^{(1)}\cdot\mathbf{Q}=Q, \quad \mathbf{e}_\mathbf{Q}^{(\alpha)}\cdot\mathbf{Q}=0 \quad \text{for} \quad \alpha=2,3. \quad (5)$$

In other words the ionic displacements are conveniently decomposed into longitudinal and transverse modes since in the long-wavelength limit only the longitudinal modes couple to the electrons. From the definition of $\beta(\mathbf{K},\mathbf{k},w)$, we have

$$\int d^3r'd^3k'\ V(\mathbf{R}_j^0-\mathbf{r}')\tilde{F}_1(\mathbf{r}',\mathbf{k}',t)$$
$$=\int d^3Kdw\ \exp[i(\mathbf{K}\cdot\mathbf{R}_j^0-wt)]\phi(\mathbf{K})$$
$$\times\int d^3k'\ \beta(\mathbf{K},\mathbf{k}',w), \quad (6)$$

so that the elimination of $\beta$ from Eq. (3), by expressing it with the aid of Eq. (1) in terms of the expectation value $\langle\Omega|\mathbf{a}_j|\Omega\rangle$, will eventually yield a nonlinear Schrödinger equation for the phonon state vector $\Omega(t)$. In order to obtain this equation which will ultimately determine the possible eigenfrequencies for the sound waves, we first have to determine $\beta$ from Eq. (1) in terms of the ionic interaction. This is very easy if the exchange term [the second term on the right-hand side of Eq. (1)] were missing. On the other hand, with this term an exact solution of Eq. (1) is impossible. Fortunately, however, the exchange term is small in the long-wavelength limit (i.e., in the limit $K\ll k_F$, where $k_F$ is the wave vector of an electron at the Fermi surface). We are therefore allowed to perform a perturbation calculation treating the exchange term as small (of first order). We therefore put

$$\beta=\beta_0+\beta_1, \quad (7)$$

where $\beta_0$ is the solution of Eq. (1) without exchange, and $\beta_1$ the first-order correction. It will be seen that this approximation is an excellent one indeed. We will not go into the details of the calculation[5] but quote the final result:

$$\int d^3k[\beta_0(\mathbf{K},\mathbf{k},w)+\beta_1(\mathbf{K},\mathbf{k},w)]$$
$$=[-i/(2\pi)^4]K^2\phi(\mathbf{K})[1-w_P^2A(\mathbf{K},w)]^{-1}$$
$$\times\int dt\ e^{iwt}\sum_j\langle\Omega(t)|\mathbf{a}_j|\Omega(t)\rangle\cdot\mathbf{K}$$
$$\times\exp(-i\mathbf{K}\cdot\mathbf{R}_j^0)\{(1/m)A(\mathbf{K},w)$$
$$-w_P^2/2\hbar K^2[1-w_P^2A(\mathbf{K},w)]^{-1}B(\mathbf{K},w)\}, \quad (8)$$

with the definitions

$$A(\mathbf{K},w)=\int d^3k\frac{F_0(\mathbf{k})}{[w-(\hbar/m)\mathbf{K}\cdot\mathbf{k}]^2-[(\hbar/2m)K^2]^2}, \quad (9)$$

and

$$B(\mathbf{K},w)=\int d^3kd^3k'|\mathbf{k}-\mathbf{k}'|^{-2}\Delta F_0\Delta F_0'\frac{\mathbf{K}\cdot(\mathbf{k}-\mathbf{k}')}{[-w+(\hbar/m)\mathbf{K}\cdot\mathbf{k}+(\hbar/2m)K^2]^2[-w+(\hbar/m)\mathbf{K}\cdot\mathbf{k}'+(\hbar/2m)K^2]}. \quad (10)$$

It is well known[6] that the expression $1-w_P^2A=\epsilon$ is just the dielectric constant of an electron gas in the self-consistent field approximation so that indeed the ion-electron interaction potential $\phi(\mathbf{K})$ is greatly reduced by the screening due to the electrons, $\phi(\mathbf{K})$ in Eq. (8) being replaced by $\epsilon^{-1}\phi(\mathbf{K})$. Now inserting Eq. (8) into Eq. (6) and utilizing Eq. (4), we obtain after straightforward calculation, confining ourselves to the long wavelength limit (i.e., neglecting all umklapp contributions), the following expression for the interaction Hamiltonian of Eq. (3):

$$H_{\text{inter}}=\frac{\hbar N_1^2}{4\pi mM}\sum_\mathbf{Q}\int dt'dw\ e^{iw(t'-t)}Q^4[\phi(\mathbf{Q})]^2$$
$$\times[1-w_P^2A(\mathbf{Q},w)]^{-1}[w_1(\mathbf{Q})]^{-1}$$
$$\times\left\{A(\mathbf{Q},w)-\frac{mw_P^2}{2\hbar Q^2}[1-w_P^2A(\mathbf{Q},w)]^{-1}B(\mathbf{Q},w)\right\}$$
$$\times[b_1(\mathbf{Q})-b^\dagger(-\mathbf{Q})]$$
$$\times\langle\Omega(t')|b_1^\dagger(\mathbf{Q})-b_1(-\mathbf{Q})|\Omega(t')\rangle. \quad (11)$$

As we said earlier, only the longitudinal modes contribute in the long-wavelength limit. Equation (3), with the interaction term replaced by expression (11),

[5] A reader interested in mathematical details here and in the following, is referred to O. von Roos, Technical Report 32-106, Jet Propulsion Laboratory, California Institute of Technology (unpublished).

[6] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. 28, 8 (1954).

is then the nonlinear Schrödinger equation we were looking for. It is now convenient to transform this equation into the density matrix language in the occupation number formalism. We then have, dropping the index on the creation and destruction operators,

$$\langle\Omega(t)|b^\dagger(\mathbf{Q}_l)-b(-\mathbf{Q}_l)|\Omega(t)\rangle = \mathrm{Tr}\{\rho(t)[b^\dagger(\mathbf{Q}_l)-b(-\mathbf{Q}_l)]\}, \quad (12)$$

with

$$\rho=\rho(N_j|N_j',t), \quad (13)$$

the density matrix in the occupation number formalism. Here $N_j$ is short for

$$N_j\equiv N_1N_2N_3\cdots N_j\cdots,$$

an array of arbitrary positive integers such that $N_j=3$, for instance, means that there are 3 phonons with wave vector $\mathbf{Q}_j$. In this representation we have

$$b(\mathbf{Q}_l)\equiv b_l(N_j|N_j')=(N_l')^{\frac{1}{2}}\delta(N_j|N_j'-\delta_{jl}), \quad (14)$$

$$b^\dagger(\mathbf{Q}_l)\equiv b_l^\dagger(N_j|N_j')=(N_l'+1)^{\frac{1}{2}}\delta(N_j|N_j'+\delta_{jl}), \quad (15)$$

where of course $\delta(N_j|N_j')$ is a product of Kronecker symbols:

$$\delta(N_j|N_j')=\delta(N_1|N_1')\delta(N_2|N_2')\cdots\delta(N_i|N_i')\cdots.$$

From Eqs. (13)–(15), we have for the trace Eq. (12)

$$\mathrm{Tr}\{\rho[b^\dagger(\mathbf{Q}_l)-b(-\mathbf{Q}_l)]\} = \sum_N\{(N_l+1)^{\frac{1}{2}}\rho(N_j|N_j+\delta_{jl},t) - (N_{-l})^{\frac{1}{2}}\rho(N_j|N_j-\delta_{j-l},t)\}, \quad (16)$$

where the sum runs over all possible positive integers $N$ for each $j$. It is now easy to translate the Schrödinger equation (3) into a von Neumann equation. In fact, we have

$$i\hbar\partial\rho/\partial t=H\rho-\rho H, \quad (17)$$

which yields, after performing the appropriate matrix multiplications, with the definitions (32)–(35),

$$\begin{aligned}
&i\hbar\frac{\partial}{\partial t}\rho(N_j|N_j',t)\\
&=[E(N_j)-E(N_j')]\rho+\frac{\hbar N_1^2}{4\pi mM}\int dt'dw\, e^{iw(t'-t)}\sum_l Q_l^4[\phi(\mathbf{Q}_l)]^2[1-w_P^2A(\mathbf{Q}_l,w)]^{-1}[w,(\mathbf{Q}_l)]^{-1}\\
&\times\left\{A(\mathbf{Q}_l,w)-\frac{mw_P^2}{2\hbar Q_l^2}[1-w_P^2A(\mathbf{Q}_l,w)]^{-1}B(\mathbf{Q}_l,w)\right\}\sum_{N''}\{(N_l''+1)^{\frac{1}{2}}\rho(N_j''|N_j''+\delta_{jl},t')-(N_{-l}'')^{\frac{1}{2}}\rho(N_j''|N_j''-\delta_{j-l},t')\}\\
&\times[(N_l+1)^{\frac{1}{2}}\rho(N_j+\delta_{jl}|N_j',t)+(N_{-l}'+1)^{\frac{1}{2}}\rho(N_j|N_j'+\delta_{j-l},t)-(N_{-l})^{\frac{1}{2}}\rho(N_j-\delta_{j-l}|N_j',t)\\
&\qquad-(N_l')^{\frac{1}{2}}\rho(N_j|N_j'-\delta_{jl},t)]. \quad (18)
\end{aligned}$$

Equation (18) may be called the collisionless Boltzmann equation for the phonons. It has the properties any collisionless Boltzmann equation must have: First, any diagonal time-independent matrix satisfies Eq. (18) identically; second, the entropy

$$S=\mathrm{Tr}\{\rho\ln\rho\} \quad (19)$$

is a constant of the motion. Particularly, the density matrix of thermal equilibrium,

$$\rho_0=Z^{-1}\exp[-\hbar\beta\textstyle\sum_j w_1(\mathbf{Q}_j)N_j]\delta(N_j|N_j'), \quad (20)$$

with

$$Z=\textstyle\sum_N\exp[-\hbar\beta\sum_j w_1(\mathbf{Q}_j)N_j], \quad (21)$$

satisfies Eq. (18) identically. The assumption that the major part of the phonons is in thermal equilibrium, so that we may put

$$\rho=\rho_0+\rho_1, \quad (22)$$

where $\rho_1\ll\rho_0$ and $\rho_0$ is given by Eq. (20) achieves again a linearization of Eq. (18) in complete analogy to the electron case.[2] Introducing the Fourier transform,

$$\rho_1(N_j|N_j',w)=1/2\pi\int dt\, e^{iwt}\rho_1(N_j|N_j,t), \quad (23)$$

we obtain after linearization the following equation for $\rho_1$:

$$\begin{aligned}
&[\hbar w+E(N_j')-E(N_j)]\rho_1(N_j|N_j',w)\\
&=\frac{\hbar N_1^2}{2mM}\sum_l Q_l^4[\phi(\mathbf{Q}_l)]^2[w_1(\mathbf{Q}_l)]^{-1}[1-w_P^2A(\mathbf{Q}_l,w)]^{-1}\left\{A(\mathbf{Q}_l,w)-\frac{mw_P^2}{2\hbar Q_l^2}[1-w_P^2A(\mathbf{Q}_l,w)]^{-1}B(\mathbf{Q}_l,w)\right\}\\
&\times\sum_{N''}\{(N_l''+1)^{\frac{1}{2}}\rho_1(N_j''|N_j''+\delta_{jl},w)-(N_{-l}'')^{\frac{1}{2}}\rho_1(N_j''|N_j''-\delta_{j-l},w)\}[(N_l+1)^{\frac{1}{2}}\rho_0(N_j+\delta_{jl}|N_j')\\
&\qquad+(N_{-l}'+1)^{\frac{1}{2}}\rho_0(N_j|N_j'+\delta_{j-l})-(N_{-l})^{\frac{1}{2}}\rho_0(N_j-\delta_{j-l}|N_j')-(N_l')^{\frac{1}{2}}\rho_0(N_j|N_j'-\delta_{jl})]. \quad (24)
\end{aligned}$$

Since $\rho_0$ is diagonal, we see immediately that if the set $N_j$ differs from the set $N_j'$ by more than one unit or not at all, then $\rho_0 \equiv 0$. Utilizing this fact it is not difficult to discover that Eq. (24) allows for nontrivial solutions only if the frequency $w$ satisfies the following dispersion relation:

$$w^2=[w_1(\mathbf{Q})]^2+\frac{N_1^2}{mM}Q^4[\phi(\mathbf{Q})]^2\frac{A(\mathbf{Q},w)}{1-w_P^2A(\mathbf{Q},w)}\left\{1-\frac{mw_P^2}{2\hbar Q^2}\frac{B(\mathbf{Q},w)}{A(\mathbf{Q},w)[1-w_P^2A(\mathbf{Q},w)]}\right\}. \tag{25}$$

The second term in the curly bracket of expression (25) is due to exchange. If it is omitted, formula (25) becomes identical with the dispersion relation of Bardeen and Pines.[4] We also see that the temperature dependence of $w$ is determined by the Fermi-Dirac distribution $F_0(\mathbf{k})$, used in the definition of $A$ and $B$. Without actually calculating the integrals (9) and (10), it can be seen, however, that the temperature effect is small for moderate temperatures since $F_0(\mathbf{k})$, at temperature $T°$, deviates appreciably from the distribution at 0°K only at the Fermi surface but contributions to the integrals (9) and (10) are small in this region.

### 3. DISCUSSION OF THE EXCHANGE CONTRIBUTION

In the long-wavelength limit, the integrals $A$ and $B$ may be computed easily using the 0°K distribution for $F_0(\mathbf{k})$. The result is

$$A(\mathbf{Q},w)=-3(v_FQ)^{-2}, \tag{26}$$

$$B(\mathbf{Q},w)=8\pi^2(3/4\pi k_F^3)^2(m/\hbar)^3, \tag{27}$$

independent of $w$. $v_F$ is the velocity at the surface of the Fermi sphere. With these approximations, formula (28) goes over into

$$w^2=[w_1(\mathbf{Q})]^2-\frac{N_1^2}{mMw_P^2}Q^4[\phi(\mathbf{Q})]^2\times\left\{1-\frac{v_F^2Q^2}{3w_P^2}+\frac{1}{4}\frac{Q^2}{k_F^2}\right\}, \tag{28}$$

keeping only terms of lowest order in $Q$. We see immediately that the last two terms in the curly bracket (the last term is due to exchange) are of the same order of magnitude since $v_F/w_P\approx k_F^{-1}\approx 10^{-8}$ cm. An expression for the elastic constants of sodium in terms of the frequencies of sound is given by Bardeen and Pines[4] (Appendix A). Repeating their calculations with expression (28), it is found that the elastic constants are given by

$$c_{11}+2c_{44}=N_1\left\{\frac{2}{3}E_F+\frac{6}{10}\frac{e^2}{v_S}-2\gamma[V(r_S)-E_0]-\frac{\pi e^2N_1}{k_F^2}\right\}, \tag{29}$$

where the last term constitutes the exchange contribution. Taking the values of reference 4 for the Fermi energy $E_F$, etc., we have from Eq. (29)

$$c_{11}+2c_{44}=2.6\times10^{22}(9.3-2.1)\times10^{-12}=1.9\times10^{11}\ \text{erg/cm}^3,$$

which is 10% lower than the experimental value:

$$c_{11}+2c_{44}=2.13\times10^{11}\ \text{erg/cm}^3,$$

and 20% lower than the corresponding value without exchange:

$$c_{11}+2c_{44}=2.4\times10^{11}\ \text{erg/cm}^3.$$

Finally, comparing the exchange correction in Eq. (28) with the corresponding one for the plasma oscillations,[7] it is found that the correction in case of the sound waves is slightly larger (by a factor of 5/3) than in the case of plasma oscillations.

In conclusion we would like to draw attention to a recent paper by Hone[8] in which exchange and correlation corrections to the electron-phonon interaction are calculated within the framework of the Bohm and Pines approach. However, it is difficult to compare the present results with those of Hone since his results depend on a Fermi-Thomas screening factor introduced somewhat *ad hoc*. The calculations of the present paper are only valid in the long-wavelength limit. Otherwise there would be a mixing with the transverse modes of lattice vibrations and correlation effects would become important. Correlation effects (deviations from the Hartree-Fock approximation) are currently under investigation.

[7] O. von Roos, Phys. Rev. **121**, 941 (1961), where a list of earlier references can be found.

[8] D. Hone, Phys. Rev. **120**, 1600 (1960).